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The emission spectrum of indium monobromide

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[Plate—12–13]

The emission band spectrum of indium monobromide is excited in a radio frequency discharge from a 1/2kw oscillator Photographs of the spectra recorded in the first order of 21 ft concave grating spectrograph revealed many more new bands in the region $\lambda 3980-\lambda 3560$Å, where two band systems A and B were reported earlier in absorption Vibrational analyses of these two band systems are considerably extended to include all the new bands observed in the present investigation. The following vibrational formulae are derived for the P heads of $In^{79}Br$ molecule. The two sub-systems are found to be the components of the $^3\Pi_{0,1}-X^1\Sigma^+$ transition of the InBr molecule.

System A

$$\nu = 26595\ 60+229\ 2(v'+1/2)-1\ 42(v'+1/2)^2-223\ 1(v''+1/2)+0.56(v''+1/2)^2$$

System B

$$\nu = 27379\ 44+225\ 0(v'+1/2)-1.53(v'+1/2)^2-223.0(v''+1/2)+0.59(v''+1/2)^2$$

Introduction

The emission band spectrum of InBr was first reported by Patrikalu & Hochberg (1933) to consist of a series of bands extending in the regions $\lambda 3980-\lambda 3590$Å and $\lambda 3050-\lambda 2850$Å. Later Wehrli & Miescher (1934) studied the absorption spectrum of InBr in the 2nd order dispersion of a 3-meter grating. The bands in the region $\lambda 3050-\lambda 2850$ Å were designated as system C The discrete bands in the region $\lambda 3850-\lambda 3560$Å were analysed as belonging to two sub-systems A and B and attributed to $^3\Pi_0-X^1\Sigma^+$ and $^3\Pi_1-X^1\Sigma^+$ transitions respectively of InBr Following our recent work on the analogous triplet systems of AlBr (Lakshminarayana & Haranath 1970a) and AlI (Lakshminarayana & Haranath 1970b), it was thought worthwhile to re-investigate the emission spectrum of InBr in higher dispersion with the object of gaining more information on the vibrational structure of these band systems The results of the present investigation are described here

Experimental

Pure indium metal pellets are spread inside a translucent silica discharge tube provided with a side tube at one of its ends. A small bulb containing fuming liquid bromine is connected to the side tube through a stopcock. In order to regulate the supply of bromine vapour the tube bulb is immersed in a suitable

low temperature bath. The other end of the discharge tube which is drawn into an adapter is connected to a high vaccum pump through a liquid air trap. The tube is excited by R.F discharge from a 500 watt oscillator operating at 30-40MHz. When a regulated supply of bromine is passed over the heated metal a characteristic bluish discharge is observed Photographs of the spectrum are taken on Hilger $\mathbf{E}_1$ Quartz Littrow spectrograph and in the first order of a 21 ft concave grating spectrograph (dispersion 1.25Å/mm) Kodak 103-a0 plates are used to record the spectra in the first order of the grating spectrograph giving an exposure of one hour duration

Results and analysis

Wehrli & Miescher (1934) reported the vibrational analysis of the bands of InBr in the region $\lambda 3850-3560$Å as belonging to two sub-systems designated as *A* and *B* The bands of system *A* are observed to be single headed (*P* heads) and attributed to $^3\Pi_0 - X^1\Sigma^+$ transition while the bands of system *B* were observed to be double headed (*P* and *Q*) and attributed to a $^3\Pi_1 - X^1\Sigma^+$ transition When the spectrum was excited in a radio frequency discharge from a 500 watt oscillator it was found that systems *A* and *B* were more extensively developed than in absorption. About 240 bands could be observed in both the systems as against 110 bands observed in absorption The two systems photographed in the first order of a 21 ft concave grating spectrograph are shown in plate 12, figure 1. It is observed that the higher sequences belonging to both the systems were very well developed in the present emission photographs

System A. The different sequences of system *A* were identified as shown in figure 1. Of these, the bands of sequences $\Delta v = -3$, -4, -5 and -6 are newly obtained in the present work In addition some new bands belonging to the other sequences were also observed. As the bands are degraded towards shorter wavelengths the heads are identified as *P* heads These *P* heads were observed to be double due to the bromine isotope effect The following vibrational formula was derived for the *P* heads of $In^{79}Br$ molecule

$$\nu = 26595.60+229.2(v'+1/2)-1.42(v'+1/2)^2-223.1(v''+1/2) \\ +0.56(v''+1/2)^2$$

The vibrational assignments and wavenumbers of the additional bands observed in the present work of this system are shown in table 1a. The agreement between the observed and calculated wavenumbers using the above formula is found to be satisfactory as shown in the last column of table 1a

System B. The different sequences of system *B* were identified as shown in figure 1. Of these, the bands of sequences $\Delta v = -4$, -5, are newly obtained in the present work. In addition some more new bands belonging to other sequences

were also observed. The bands of this system which are degraded to shorter wavelengths are observed to be double headed consisting of P and Q heads. The P heads are sharp and line-like while the Q heads are broad and diffuse.

Table 1a. The newly observed bands in system A of $In^{79}Br$ molecule

Wavenumber cm^{-1}	Intensity	Classification v', v''	$\nu_{obs} - \nu_{cal}$ cm^{-1}
25321.2	1	5, 11	−0.4
25509 5	1	1,6	−0.2
25517.4	2	2,7	−0.6
25523.9	3	3,8	−0.6
25528 7	3	4,9	−0 6
25531.9	4	5,10	−0.5
25726.2	2	1,5	+0.1
25733.4	3	2,6	+0 2
25738.3	4	3,7	−0.3
25741.8	6	4,8	−0.5
25936.2	4	0,3	+0 2
25943 8	5	1,4	+0.2
26727 1	3	13,12	−2.1
26824 5	9	1,0; 4,3	+0.3
26825.9	8	2,1; 3,2	−0 3
27044 3	6	4,2	+0 3
27046.8	6	3,1	−0.2
27048.0	7	2,0	−0.3
27187 8	6	11,8	+0.1

Under the high dispersion used in the present work (1.25Å/mm) the bands of $\Delta v = +1$ and $+2$ sequences were clearly resolved down to low values of v' and v'' as shown in figure 2 (plate 13). According to the present vibrational analysis, the vibrational assignments of bands in the $\Delta v = +1$, $+2$ sequences as reported by Wehrli & Miescher (1934) have to be increased by two units and in $\Delta v = +3$ sequence by one unit, both in the upper and lower states. The detailed classifications of these bands in the $\Delta v = +1$ and $+2$ sequences are shown in Plate 13, figure 2. These vibrational assignments were confirmed by a detailed

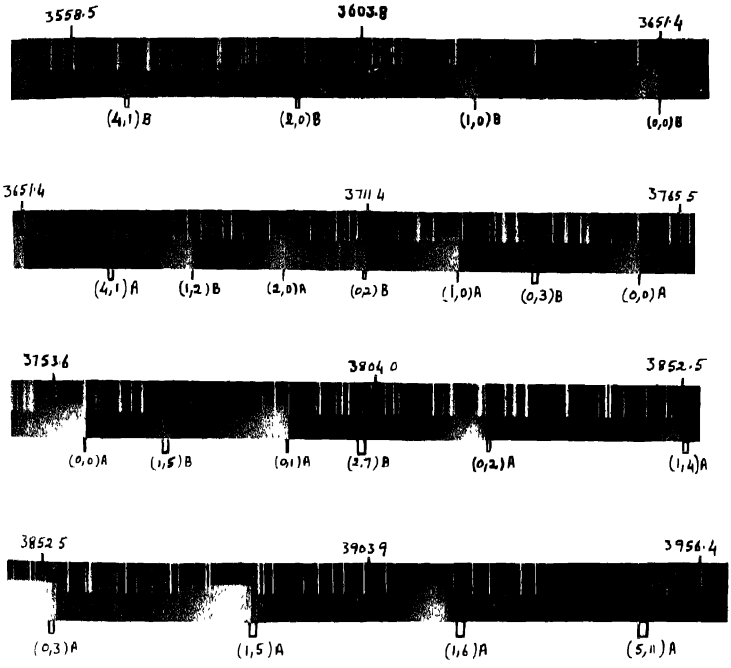

Figure 1. *A* and *B* systems of InBr (21 ft concave grating spectrogram)

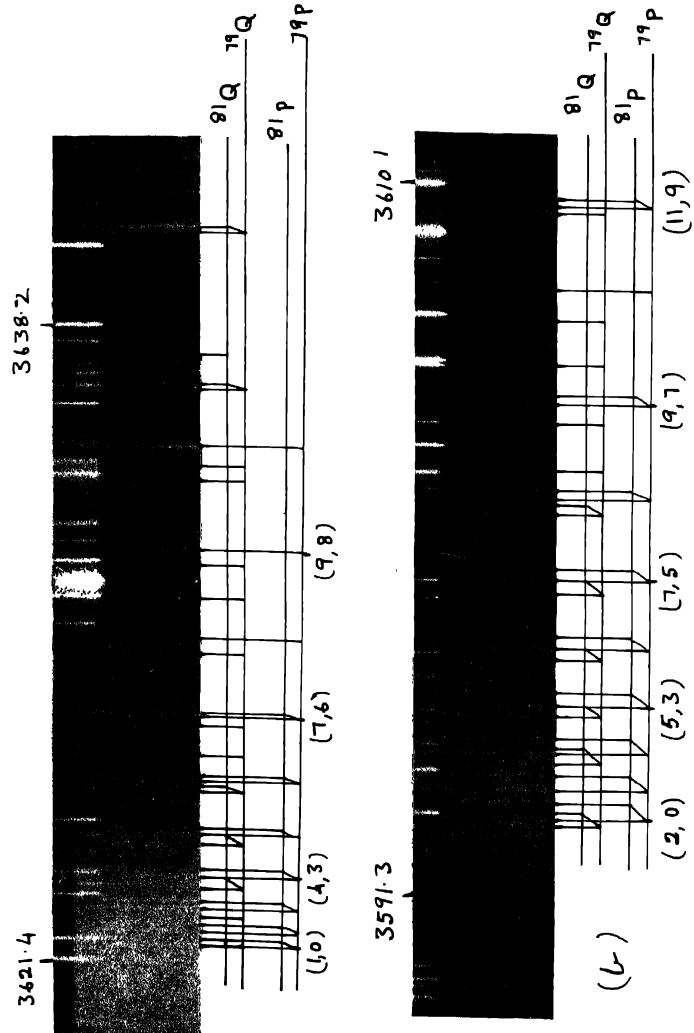

Figure 2. (a) The (1,0) sequence of system *B* of InBr
(b) The (2,0 sequence of system *B* of InBr

study of the bromine isotopic effect. The following new vibrational quantum formula for the P heads of In ^{79}Br molecule is derived :

$$\nu = 27379.44 + 225.0(v'+1/2) - 1.53(v'+1/2)^2 - 223.0(v''+1/2) + 0.59(v''+1/2)^2$$

From the present analysis it is observed that $\omega_e' > \omega_e''$ as in system A while according to the analysis proposed by Wehrli & Miescher $\omega_e' < \omega_e''$. The vibrational frequencies of $^3\Pi_0$ and $^3\Pi_1$ levels are close to each other as expected for the components of a $^3\Pi$ level.

The wavenumbers and their vibrational assignments of P, Q and Q' heads of the newly observed bands of In^{79}Br molecule of this system are given in table 1b. A peculiar feature of this system is that in the $\Delta v = +3$, $+2$ and $+1$ sequences the bands are degraded towards longer wavelengths while the sequences are degraded to shorter wavelengths. It is observed in some bands with high values of v' and v'' that the Q branch tends to form another head which is degraded to longer wavelengths as shown in figure 2. These heads are classified as Q' heads in table 1b.

As can be seen from the figures 1 and 2, the band heads exhibit well-resolved bromine isotope effect. The observed shifts of the band heads due to the In^{81}Br molecule from those of the slightly more abundant In^{79}Br molecule, agree well with those calculated as can be seen from table 2. This isotope study confirms the present changes in the vibrational assignments of some of the bands.

By analogy with similar band systems of the related molecules InF, InCl the common lower state of the two sub-systems is identified as ground state $X^1\Sigma'$ arising from the configuration

$$\ldots(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 \ldots X^1\Sigma^+.$$

and the upper $^3\Pi_{0,1}$ states to the following excited configuration

$$\ldots(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)\ (v\pi) \ldots {}^3\Pi_r, {}^1\Pi.$$

of the InBr molecule. Thus the two sub-systems of the InBr molecule may be designated as a $^3\Pi_{0,1} - X^1\Sigma^+$ systems.

Table 1b. The newly observed bands in system B of $In^{79}Br$ molecule.

Wavenumber cm^{-1}	Intensity	Classification v', v''	Band Head	$\nu_{obs}-\nu_{cal}$ cm^{-1}
26292.0	2	2,7	P	−1.1
26505.9	2	1,5	P	+1.1
26723.8	2	2,5	P	+0.1
27532.6	4	9,8	Q'	
27558.4	3	7,6	Q	
27563.5	3	7,6	Q'	
27569.2	5	6,5	P	+0.6
27571.9	3	6,5	Q	
27574.0	2	6,5	Q'	
27581.5	2	5,4	Q	
27588.0	5	4,3	P	+0 3
27590.1	3	4,3	Q	
27594.5	6	3,2	P	+0.1
27596.4	2	3,2	Q	
27599.3	7	2,1	P	+0 1
27602.2	8	1,0	P	0
27749 7	2	9,7	Q'	
27767 9	1	8,6	Q'	
27788.8	3	6,4	Q	
27793.7	1	6.4	Q'	
27797.0	6	5,3	P	+0.5
27800.1	3	5,3	Q	
27809.8	2	4,2	Q	
27814.0	2	3,1	Q	
27815.2	6	3,1	P	+0.2
27821.0	7	2,0	P	0
27822.7	2	2,0	Q	
27954.5	2	9,6	P	+0.2
27975.9	2	8,5	Q	
27993.0	2	7,4	Q	
28007.7	3	6,3	Q	
28019.8	3	5,2	Q	
28028.0	6	4,1	P	+0.2
28030 3	3	4,1	Q	
28036.8	5	3,0	P	0
28039.0	3	3,0	Q	

Table 2. Bromine isotope effect

	v', v''	Shift (cm^{-1}) Obs.	Cal.	v', v''	Shift (cm^{-1}) Obs.	Cal.
System A						
	5,11	9.4	9.2	4,3	1.6	1.5
	1,6	7.5	7.8	3,2	1.5	1 6
	2,7	7 4	7.7	2,1	1.5	1.6
	3,8	7 1	7.7	1,0	1.6	1.5
	4,9	7.3	7.6	12,10	1.7	1 5
	5,10	7.5	7.7	11,9	1.7	1 9
	1,5	6.2	6 3	10,8	2.1	2.0
	2,6	5.6	6.1	9,7	2.4	2.3
	4,8	6.3	6 2	8,6	2.4	2.5
	0,3	4.8	4.8	7,5	2 6	2.7
	1,4	4.8	4.7	6,4	2.9	2 9
	2,5	4.8	4 7	5,3	3.1	3.0
	3,6	4.5	4.7	4,2	3.5	3.1
	0,2	3.3	3 2	3,1	3.2	3.2
	1,3	3.2	3.1	2,0	3.2	3.3
	2,4	3.0	3.1	11,8	3.2	3.3
	3,5	2.9	3 1	10,7	3.5	3.6
	4.6	2 9	3 1	9.6	4.2	3.8
	0,1	1.6	1.6	8,5	4.3	4.0
	1,2	1.6	1 5	7,4	4 3	4.2
	2,3	1.7	1.5	6,3	4.5	4.4
	8,7	1 1	1.0	5,2	5.0	4 6
	7,6	1.5	1.2	4,1	4.7	4 7
	6,5	1 5	1.3			
	5,4	1 3	1.4			
System B						
	2,7	7.1	7.8	8,6	2.1	2.2
	1,5	6.8	6.3	7,5	2.4	2 4
	1,4	4.9	4.8	6,4	2.7	2.6
	2,5	4.7	4.7	5,3	2 9	2.8
	0,2	3.4	3.2	4,2	3 2	3.0
	1,3	3.3	3.2	3,1	3.1	3.1
	7,6	1.3	0.9	2,0	3.3	3.2
	6,5	1.2	1.1	9,6	3.8	3.4
	5,4	1.2	1.2	8,5	3.3	3.7
	4,3	1.6	1.4	7,4	3.7	3.9
	3,2	1.3	1.5	6,3	4.3	4.2
	2,1	1.6	1.5	5,2	4.5	4.4
	1,0	1.6	1.6	4,1	4.6	4.6
	9,7	1.6	1.9	3,0	4.8	4.7

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